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# THE STABILITY OF THE FERROMAGNETIC STATE IN $\text{La}(\text{Fe}_{0.86}\text{Al}_{0.14})_{13}$ UNDER HIGH PRESSURE

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The ferromagnetic (FM)  $\text{La}(\text{Fe}_{0.86}\text{Al}_{0.14})_{13}$  Invar alloy displays a pressure-induced FM to antiferromagnetic (AF) phase transition at a pressure as low as  $p \lesssim 0.1$  GPa. A quantitative analysis of the results shows that the FM  $\rightarrow$  AF magnetic phase transition recently observed in  $\text{La}(\text{Fe}_x\text{Al}_{1-x})_{13}$  at ambient pressure is governed by the decrease of the unit cell volume rather than the increase of the number of Fe nearest neighbor atoms.

## INTRODUCTION

THE STUDY OF ITINERANT MAGNETISM in Fe-based materials in connection with the Invar problem is fundamental in understanding the ferromagnetism of 3d-metals and alloys [1]. Among the class of magnetic materials which show *Invar behavior* (e.g. Fe–Ni [2], Fe–Pt [3] alloys), a new intermetallic system,  $\text{La}(\text{Fe}_x\text{Al}_{1-x})_{13}$ , has been recently discovered [4]. This intermetallic series has the cubic  $\text{NaZ}_{13}$  ( $D_{2d}$ ) structure, which can be stabilized with Fe concentration,  $x$ , between 0.46 and 0.92, where the lattice parameter ( $a$ ) decreases linearly with increasing  $x$  [4]. It has been found by macroscopic (a.c. susceptibility, magnetization, and electrical resistivity) [4] as well as by microscopic ( $^{57}\text{Fe}$  Mössbauer effect (ME) [5] studies that the series exhibits a most unusual magnetic phase diagram (Fig. 1) consisting of three different types of magnetic order: (i) a mictomagnetic (MM) state at low Fe concentration, (ii) a soft ferromagnetic (FM) state at high Fe concentration; and (iii) an antiferromagnetic (AF) state at highest Fe concentration.

The average magnetic hyperfine (h.f.) field,  $\bar{B}_{\text{eff}}$ , deduced from the ME measurements shows an abrupt decrease in going from the FM ( $x = 0.86$ ) to the AF ( $x = 0.88$ ) state, indicating the sensitivity of  $\bar{B}_{\text{eff}}$  to a change of the spin structure in this system [5]. Regarding the Invar effect, it has been shown that the system exhibits a zero thermal expansion coefficient at about

240 K for samples near the instability region of the FM order ( $x = 0.81, 0.86$  and  $0.89$ ) [4]. This fact lets suggest [4, 5] that the unusual collapse of the FM state, ending with a FM  $\rightarrow$  AF transition at the highest Fe concentration ( $0.86 \leq x \leq 0.92$ , s. Fig. 1), has

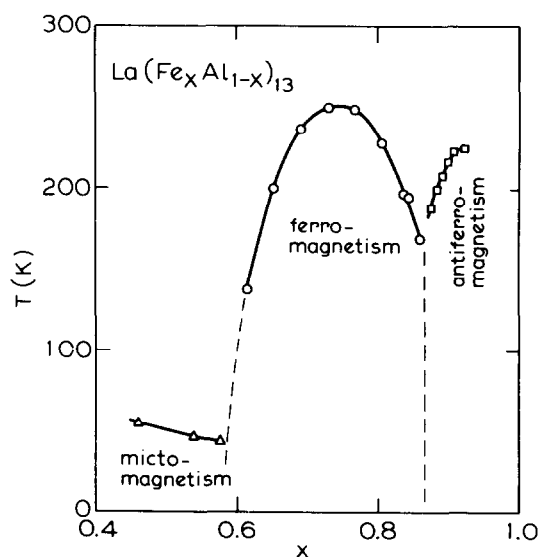


Fig. 1. Magnetic phase diagram of  $\text{La}(\text{Fe}_x\text{Al}_{1-x})_{13}$  after [4]. The freezing temperature is indicated by  $\Delta$ , The Curie temperature ( $T_C$ ) by O, and the Néel temperature ( $T_N$ ) by  $\square$ . The vertical dashed line at  $x \approx 0.86$  denotes the phase boundaries between the FM and AF states.

the same origin as in FM f.c.c. Fe–Ni and Fe–Ni–Mn alloys [6, 7]. Here it has been shown that the surrounding of the nearest neighbors (*nn*) for one of the two Fe sites in  $\text{La}(\text{Fe}_x\text{Al}_{1-x})_{13}$ ,  $0.81 \leq x \leq 0.92$  is very similar to that in  $\gamma$ -Fe or f.c.c. Fe–Ni Invar alloys [8]. Although the above arguments suggest a qualitative but consistent picture for the magnetic behavior of the system, we want to show how high pressure can give a deeper insight into the *nature* of both the FM  $\rightarrow$  AF transition and the magnetic ground state in this system.

Concerning the problem of the FM  $\rightarrow$  AF phase transition one has to consider two *superimposed* effects, when going from the FM ( $x = 0.86$ ) to AF ( $x = 0.88$ ) state: (a) an increase in the concentration,  $x$ , i.e. increase in the number of Fe *nn*; (b) a decrease of the lattice parameter, i.e. a decreasing unit cell volume. Thus, a promising approach to achieve a better understanding of the nature of the FM  $\rightarrow$  AF phase transition is to separate these two effects by applying external pressure, while the chemical composition remains unchanged.

## RESULTS

We have performed  $^{57}\text{Fe}$  high-pressure ME experiments ( $^{57}\text{Co}$ : Rh source) on the FM  $\text{La}(\text{Fe}_{0.86}\text{Al}_{0.14})_{13}$  alloy at 4.2 K and up to pressures of 2.4 GPa. The high-pressure setup is described elsewhere [9]. The investigated samples  $\text{La}(\text{Fe}_{0.86}\text{Al}_{0.14})_{13}$  ( $T_c = 168$  K) and  $\text{La}(\text{Fe}_{0.88}\text{Al}_{0.12})_{13}$  ( $T_N = 187$  K) were synthesized as described in the literature [4]. X-ray diffraction patterns at room temperature have shown the phase purity of the  $\text{NaZ}_{13}$ -type structure. The lattice parameters have been also determined at 6 K using the X-ray diffraction technique.

Figure 2 shows some typical  $^{57}\text{Fe}$  ME spectra of the FM,  $\text{La}(\text{Fe}_{0.86}\text{Al}_{0.14})_{13}$  sample at 4.2 K and at pressures of 0, 0.1 and 2.4 GPa; for comparison the ME spectrum of the AF  $\text{La}(\text{Fe}_{0.88}\text{Al}_{0.12})_{13}$  sample at ambient pressure and at 4.2 K is also shown. Small shoulders in the ME spectra observed at higher velocities ( $\approx -5$  and  $\approx +6 \text{ mm s}^{-1}$ ) are due to a small amount of  $\alpha$ -Fe in the investigated samples. All ME spectra could be fitted using a modified histogram method [10]. Some of the resulting h.f. field distributions,  $P(B_{\text{eff}})$ , for the two samples are shown in Figure 3; the h.f. field component, concentrated at  $\bar{B}_{\text{eff}} \approx 30$  T is due to  $\alpha$ -Fe impurity (see above). We observe in addition a small amount ( $\approx 11\%$ ) of h.f. field component located at about 12 T.

The most important result of our high-pressure experiments on FM  $\text{La}(\text{Fe}_{0.86}\text{Al}_{0.14})_{13}$  is the observation of a pressure induced FM  $\rightarrow$  AF phase tran-

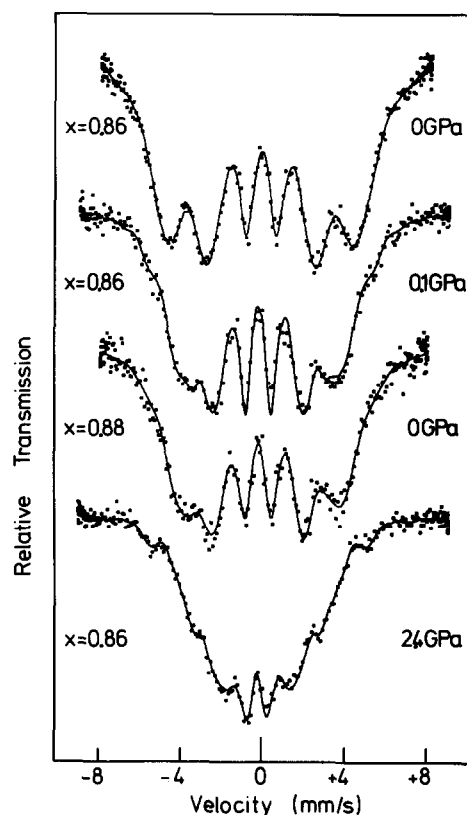


Fig. 2. Typical  $^{57}\text{Fe}$  ME spectra of  $\text{La}(\text{Fe}_{0.86}\text{Al}_{0.14})_{13}$  at  $p = 0, 0.1$  and  $2.4$  GPa and at  $4.2$  K. The ME spectrum of AF  $\text{La}(\text{Fe}_{0.88}\text{Al}_{0.12})_{13}$  at  $p = 0$  GPa and at  $4.2$  K is also shown. Shoulders in the ME spectra appearing at high velocities ( $\approx -5$  and  $\approx +6 \text{ mm s}^{-1}$ ) are due to a small amount of  $\alpha$ -Fe impurity.

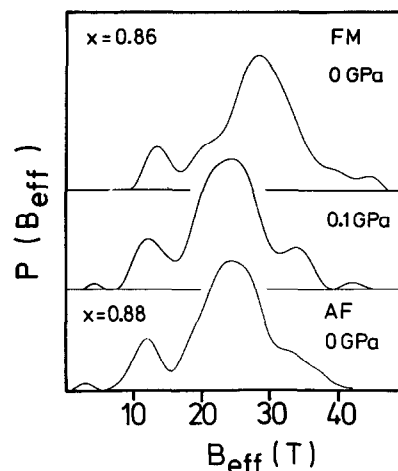


Fig. 3. Magnetic h.f. field distributions,  $P(B_{\text{eff}})$ , of  $\text{La}(\text{Fe}_{0.86}\text{Al}_{0.14})_{13}$  at  $p = 0$  and  $0.1$  GPa; and  $\text{La}(\text{Fe}_{0.88}\text{Al}_{0.12})_{13}$  at  $p = 0$  GPa. Peaks concentrated around  $\bar{B}_{\text{eff}} \approx 30$  and  $12$  T are due to the presence of  $\alpha$ -Fe impurities and the reduced magnetic moment of the Fe site, respectively (s. text).

sition at a pressure of only  $p \lesssim 0.1$  GPa, which is by far the lowest ever reported for the known Fe related systems. This finding is concluded from the abrupt pressure shift of both the value of  $\bar{B}_{\text{eff}}$  and the shape of  $P(\bar{B}_{\text{eff}})$  at  $p = 0.1$  GPa. Here we obtain values for  $\bar{B}_{\text{eff}}$  and  $P(\bar{B}_{\text{eff}})$  essentially identical with those of AF  $\text{La}(\text{Fe}_{0.88}\text{Al}_{0.12})_{13}$  at ambient pressure (see Fig. 3). Additionally, we find a large decrease of  $\bar{B}_{\text{eff}}$  in the pressure induced AF phase with increasing pressure ( $0.1 \leq p \leq 2.4$  GPa).

## DISCUSSION

First we want to discuss the low-field component in  $P(\bar{B}_{\text{eff}})$  located at about 12 T (see Fig. 3).  $\text{La}(\text{Fe}_x\text{Al}_{1-x})_{13}$  has the cubic  $\text{NaZn}_{13}$  ( $D_{2d}$ ) structure. The Fe atoms occupy two different sites,  $\text{Fe}^I$  and  $\text{Fe}^{II}$ , in the ratio 1:12. The analysis of recent neutron diffraction measurements at 4.2 K on AF  $\text{La}(\text{Fe}_{0.92}\text{Al}_{0.08})_{13}$  [5] gave a magnetic moment  $\mu = 1.10 \mu_B$  for the  $\text{Fe}^I$  atoms, while the  $\text{Fe}^{II}$  atoms have a larger moment of  $\mu = 2.14 \mu_B$ . Thus assuming similar transferred h.f. fields, one would expect that  $P(\bar{B}_{\text{eff}})$  shows an additional spectral contribution at about half of the value of the main contribution with an intensity of about 8%. This expectation is in excellent agreement with our finding: we obtain a low-field component at about 12 T with an intensity of about 11% of the main component at 30 T.

Next we want to discuss the pressure induced FM  $\rightarrow$  AF phase transition in  $\text{La}(\text{Fe}_{0.86}\text{Al}_{0.14})_{13}$ . The most efficient way to discuss this behavior is the comparison of the change of  $\bar{B}_{\text{eff}}$  (4.2 K) with lattice parameters (at 6 K) due to chemical substitution of Fe ( $0.86 \leq x \leq 0.88$ ) with those caused by applying pressure. Figure 4 demonstrates both cases. The values of  $\bar{B}_{\text{eff}}$  are corrected from the high-field component of  $\alpha$ -Fe as mentioned before. Values of low temperature lattice parameter ( $a$ ) for different concentrations are obtained from our X-ray diffraction measurements at  $T = 6$  K on samples with  $x = 0.86$  ( $a = 11.659 \text{ \AA}$ ) and  $x = 0.88$  ( $a = 11.618 \text{ \AA}$ ). The change of the lattice parameter at different pressures, for the sample with  $x = 0.86$ , is calculated using an average value of the low-temperature compressibility,  $\approx 7 \cdot 10^{-3} \text{ GPa}^{-1}$ , of Fe-based related systems [11]. A quantitative analysis of these results (see also Fig. 4) shows that the change of the lattice parameter caused by a pressure of  $p \approx 0.1$  GPa ( $\Delta a/a \approx 2.6 \cdot 10^{-4}$ ) is more than an order of magnitude smaller than the corresponding change in the lattice parameter due to chemical substitution of Fe from  $x = 0.86$  (FM) to  $x = 0.88$  (AF) ( $\Delta a/a \approx 3.5 \cdot 10^{-3}$ ). This finding demonstrates clearly that the magnetic phase transition in

this system is governed by the decrease of the unit cell volume rather than the increase of the number of Fe  $nn$  atoms.

In this connection we want to emphasize that our high-pressure results are comparable with those in Fe-based related itinerant electron systems: for example  $\text{Fe}_2\text{P}$  [12],  $\text{Hf}_{0.8}\text{Ta}_{0.2}\text{Fe}_2$  [13] and  $\text{Hf}_{0.9}\text{Ta}_{0.1}\text{Fe}_2$  [14]. In these itinerant systems a pressure induced FM  $\rightarrow$  AF phase transition is also observed at pressures of  $p \gtrsim 0.5$ ,  $0.7$ , and  $0.85$  GPa respectively. We believe that the observation of a much lower critical pressure for the FM  $\rightarrow$  AF phase transition in our system is connected with the peculiar spin structure of the AF phase in this system: Helmholdt *et al.* [5] found from neutron diffraction measurements at 4.2 K on AF  $\text{La}(\text{Fe}_{0.92}\text{Al}_{0.08})_{13}$  that the AF phase consists out of FM ordered icosahedral clusters of 13 Fe atoms (1 central  $\text{Fe}^I$  atom plus 12  $\text{Fe}^{II}$  atoms) which show FM coupling within the (1, 0, 0) plane and an AF coupling between clusters of two adjacent planes.

Finally we discuss the effect of external pressure on the AF phase ( $0.1 \leq p \leq 2.4$  GPa). We observe a large decrease of  $\bar{B}_{\text{eff}}$  with increasing external pressure,  $\text{dln}\bar{B}_{\text{eff}}/\text{d}p \approx -15 \cdot 10^{-2} \text{ GPa}^{-1}$  (Fig. 4, see also Fig. 2). In contrast  $\bar{B}_{\text{eff}}$  increases with increasing chemical pressure (Fe concentration, see Fig. 1) [4]. From this it can be concluded, that the AF state is stabilized by increasing Fe concentration (increasing number of Fe

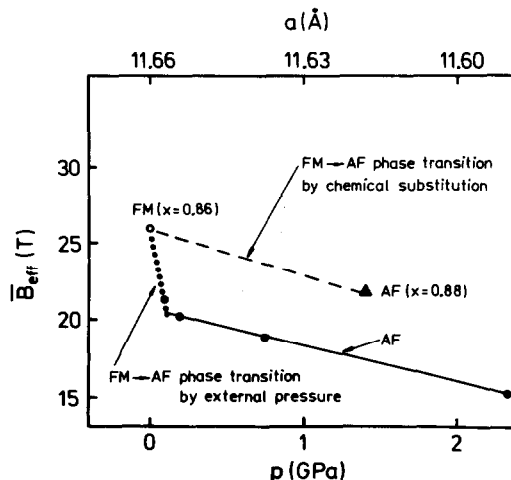


Fig. 4. Average magnetic h.f. field,  $\bar{B}_{\text{eff}}$ , at 4.2 K of  $\text{La}(\text{Fe}_x\text{Al}_{1-x})_{13}$  as a function of pressure ( $p$ ) and lattice parameter ( $a$ ): for  $x = 0.86$  (○) and  $0.88$  (▲) at ambient pressure; for  $x = 0.86$  (●) at  $p = 0.1, 0.2, 0.8$  and  $2.4$  GPa. The dashed line shows the FM  $\rightarrow$  AF phase transition due change in the chemical composition, the dotted line denotes the FM  $\rightarrow$  AF phase transition due to external pressure. The solid indicates the pressure dependence of  $\bar{B}_{\text{eff}}$  in the pressure induced AF phase.

$nn$  atoms). The large decrease of  $\bar{B}_{\text{eff}}$  with increasing external pressure is of the same order of magnitude as that found for example for FM  $\text{Fe}_{68.5}\text{Ni}_{31.5}$  Invar [15]. This last point will be the subject of further research at higher external pressures.

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